Bromine and Mixed Bromine Chlorine Oxides: Wave Function (CCSD(T) and MP2) versus Density Functional Theory (B3LYP) Calculations

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Bromine peroxide, mixed bromine and chlorine peroxides, and their isomers have been studied ab initio using both wave function and density functional theory methods. The performance of the methodologies in studying these species is analyzed. Optimized geometries, harmonic frequencies, relative energies, and isodesmic heats of formation at 0 and 298.15 K, have been calculated and used to discuss the form and relative stability of these species. The spontaneity of various possible decomposition channels for these species is also studied. Comparisons with previous ab initio calculations is presented and discrepancies are analyzed.

Introduction

In this paper we study the structure and relative stability of molecules of the types XOOY, XOYO, and XYO_2 (where X and Y stand for Cl and Br atoms), which show atmospheric interest, and continue previous research on chlorine peroxide and triatomic species involving Cl, Br, and O.[1−3]

The role of mixed bromine and chlorine peroxides and their isomers in the cycles leading to ozone depletion on the stratosphere has been put forward in several papers (see for instance refs 4−6) and is currently the subject of increasing attention. While ClOOCl has been extensively studied from the theoretical and experimental points of view using a variety of techniques, the difficulties in dealing with ClOOBr, $ClBrO_2$, and ClOBrO molecules have probably hindered the experimental work on these species, despite their potential interest, in such a way that experimental data[7] are very scarce. On the other hand, the large number of electrons involved, the high level of the theory necessary, and the large basis sets required to analyze the bonding in many of these species (particularly in the hypervalent cases) explain the lack of ab initio studies. However, there have appeared two interesting papers dealing with these molecules: a MP2/G1 work carried out by Gleghorn[8] and a density functional theory (DFT) study by Guha and Francisco,[9] which also includes G2 and CCSD(T) calculations (at the DFT optimized geometries). These works study structure and relative stability of the various isomers. The interest of these species and the technical difficulty in studying them from the ab initio point of view have led us to add to the available information and to discuss some discrepancies found with previous studies, on both the structure and energetics of some of these molecules. On the other hand, a systematic comparison between CCSD(T) and one of the most reliable DFT methods, B3LYP, seems particularly interesting in these demanding cases. The purpose of the present paper is to comply with all that mentioned above.

We have carried out a systematic comparison of the DFT results (in particular the increasingly popular B3LYP) with wave function methods MP2 in geometry optimization and show here how the choice of methodology turns out to play a substantial role in optimizing bond lengths and angles and relative stabilities. Our geometries are compared with those ab initio and experiments previously published and a discussion is carried out using the obtained geometrical parameters along with atomic charges.

Methodology

We have performed MP2 and B3LYP optimizations using the average relativistic effective potentials (AREP) (see ref 2 and quotations therein), whose reliability has been largely demonstrated. The calculations were carried out using a valence-only TZ(2df) basis set especially optimized for the AREP operators. The size of the basis set and the fact that it has been developed to be used along with AREP make this methodology rather suitable to the purpose of the present work, as we shall show below.

Study of the energetics of these molecules has also been performed at the CCSD(T) level of the theory using the previously optimized MP2/AREP-TZ(2df) geometries. All calculations have been performed using the Gaussian 94 package.[10]

Equilibrium Geometries and Frequencies

To study the equilibrium geometries, we have divided the set of molecules we considered in this work into three groups. The first one, collected in Table 1, contains the XOOY-type of molecules, namely ClOOBr, BrOOBr, and ClOOCl. The last species is included as a gauge of the dependability on the methodology we use for the peroxide forms since there are excellent experimental and theoretical studies available. As can be noticed when comparing the B3LYP bond lengths obtained by using our TZ(2df) basis set and the 6-311++G(3df,3pd) in ref 9, differences are very tiny for all the peroxide forms, always

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TABLE 1: Optimized Geometries of XOOY Molecules: BrOOBr, ClOOBr, and ClOOCl[a]

	BrOOBr			ClOOBr			ClOOCl			
	MP2 (a)	B3LYP (a)	B3LYP (b)	MP2 (a)	B3LYP (a)	B3LYP (b)	MP2 (a)	MP2 (c)	B3LYP (b)	exp (d)
XO	1.861	1.900	1.922	1.710	1.759	1.757	1.710	1.705	1.752	1.704
OO	1.410	1.359	1.335	1.412	1.363	1.347	1.416	1.412	1.370	1.426
OY				1.859	1.897	1.914				
XOO	109.6	112.6	113.3	109.0	111.5	111.8	108.9	109.0	111.4	110.1
OOY				109.4	112.4	112.8				
XOOY	82.2	84.6	85.6	82.4	84.5	86.0	82.5	82.5	84.6	81.0

[a] Key: (a) AREP-TZ(2df) calculations, this work. (b) 6-311++G(3df,3pd) calculations, ref 9. (c) EXT(f) calculations, ref 16. (d) Reference 17. Bond lengths in angstroms, bond angles in degrees.

TABLE 2: Optimized Geometries of XOYO’ Molecules: BrOBrO, ClOBrO, BrOClO, and ClOClO[a]

	BrOBrO			ClOBrO			BrOClO			ClOClO	
	MP2 (a)	B3LYP (a)	B3LYP (b)	MP2 (a)	B3LYP (a)	B3LYP (b)	MP2 (a)	B3LYP (a)	B3LYP (b)	MP2 (a)	B3LYP (a)
XO	1.846	1.854	1.867	1.703	1.710	1.699	1.843	1.874	1.895	1.700	1.720
OY	1.904	1.870	1.855	1.910	1.890	1.892	1.792	1.717	1.679	1.807	1.753
YO’	1.630	1.661	1.660	1.630	1.661	1.659	1.489	1.514	1.498	1.489	1.513
XOY	111.6	116.8	116.8	111.1	115.5	115.7	109.9	115.7	116.2	109.6	114.1
OYO’	112.0	111.1	110.3	112.2	111.4	110.4	114.2	113.6	113.6	114.5	113.9
XOYO	70.3	78.2	79.3	74.3	79.3	80.0	67.9	77.8	79.2	72.0	79.3

[a] Key: (a) AREP-TZ(2df) calculations, this work. (b) 6-311++G(3df,3pd) calculations, ref 9. Bond lengths in angstroms, bond angles in degrees.

smaller than 0.03 Å and within the reasonable expectancies for the agreement between the ab initio calculations we are comparing here. These bond length differences are nevertheless almost twice as large when the comparison MP2 versus B3LYP (using the same basis set) is carried out, but they are still small enough so as not to expect large differences in the molecular properties because of this fact. However, differences in angles, which are smaller than 1.5° in all the cases when comparing both B3LYP results in the table, grow up to 2.5 or 3° when the comparison with the MP2 results is made. These bond angle differences actually represent a noticeable distortion in the equilibrium geometries of these peroxides so that an influence on the energy differences may be expected. When the analysis above is performed on ClOOCl, one can see that bond lengths provided by the MP2 method, no matter the basis set used, are in comparable error with reference to the experimental values, and B3LYP results look somewhat poorer. Similar errors are found in all ClOO bond angles, but dihedrals provided by MP2 and B3LYP are clearly different, the error in B3LYP results being more than twice the one in MP2. The conclusion that can be drawn is that while the basis sets used in Table 1 perform comparably well, there is a clear dependence on the method in planar and dihedral angles, and in sight of the results in ClOOCl, it seems that B3LYP displays a tendency to yield dihedral angles too large.

The second group of molecules we refer to in this paper (see Table 2) is composed of straight-chain structures of the type XOYO. As was the case in the peroxides, now B3LYP provides essentially the same bond lengths when both basis sets compared in the table are used, with differences in the range of one hundredth of an angstrom, and angles, including dihedrals, also being very similar. However, differences between B3LYP and MP2 methodologies are notorious again in dihedral angles where differences range from 5 to 10° (compare columns B3LYP (a) and MP2 (a) in each molecule), that B3LYP tends toward large dihedral angles was already found in XOOY molecules. It can be noticed as well that both B3LYP calculations compared in Table 2 provide larger XOY angles than MP2 by more than 4°. But probably the most striking discrepancy between B3LYP and MP2 geometries in this family of molecules is the value of XOY angles compared to OYO. It is obvious that MP2 gives OYO angles slightly larger than XOY in BrOBrO and in ClOBrO and clearly larger in BrOClO and ClOClO, whereas B3LYP gives clearly larger XOY values than OYO in BrOBrO and ClOBrO and only slightly larger in ClOClO, BrOClO being a somewhat intermediate case. This interesting symmetrical situation cannot go without a comment. It has been argued[9] that the XOY bond angle should be expected to be larger than OYO because the lone pairs of electrons on the voluminous bromine atom would efficiently repel those on chlorine and the lone pairs on the oxygen atom in the middle would introduce further repulsion. On OYO, the argument follows, the repulsion between lone pairs on the oxygen atoms (smaller than halogens) would be small and even diminished by the resonance of BrO′ bonding electrons and the lone pairs of electrons on oxygen. In fact, this resonance $XOY{=}O \Leftrightarrow XOY^{+}O^{-}$ is apparent in both methodologies leading to OBr and OCl distances larger than those for BrO’ and ClO’. We have examined this explanation by calculating Mulliken atomic charges using MP2 and B3LYP electron densities. We found both methodologies to provide concordant charges on the atoms up to the second decimal place, which are as follows: Cl, 0.09; O, −0.32; Br, 0.60; O′, −0.37. That shows the $Y^{+}O^{-}$ character expected from one of the resonant forms, but it also displays that actually, despite the qualitative reasoning above, the repulsion between Cl and Br is expected to be smaller than OO repulsion on this molecule in sight of atomic charges, and this would lead to a value for the OBrO angle larger than that for ClOBr. That seems to be the case in the remaining molecules of this group as well, whose atomic charges are Br 0.12, O −0.33, Br 0.60, O and −0.39 for BrOBrO, with the same values, up to the second decimal place, for BrOClO, despite having a chlorine internal atom instead of a bromine one. Thus it now seems clear that OO repulsion is dominant and makes OYO clearly larger than XOY in the case where Y is a chlorine atom, being this effect being less noticeable when it is a more voluminous bromine atom.

The third type of molecule studied in this paper is composed of $BrBrO_2$, $ClBrO_2$, and $BrClO_2$ all displaying a plane of symmetry (C_s group). The basis set effect on bond distances, evaluated as the differences between both B3LYP results in

TABLE 3: Optimized Geometries of XYO_2 Molecules: $BrBrO_2$, $ClBrO_2$, $BrClO_2$, and $ClClO_2$[a]

	$BrBrO_2$			$ClBrO_2$			$BrClO_2$			$ClClO_2$		
	MP2 (a)	B3LYP (a)	B3LYP (b)	MP2 (a)	B3LYP (a)	B3LYP (b)	MP2 (a)	B3LYP (a)	B3LYP (b)	MP2 (a)	B3LYP (a)	exp (c)
XY	2.488	2.486	2.490	2.325	2.325	2.315	2.440	2.414	2.416	2.279	2.257	2.22
YO	1.595	1.618	1.618	1.591	1.613	1.613	1.441	1.460	1.445	1.441	1.453	1.44
XYO	104.1	104.8	111.4	103.6	104.2	103.7	104.5	105.0	114.7	103.8	104.5	103.5
OYO	112.1	111.5	104.2	112.1	111.5	111.3	115.0	114.6	104.7	115.2	114.4	116

[a] Key: (a) AREP-TZ(2df) calculations, this work. (b) 6-311++G(3df,3pd) calculations, ref 9. (c) Reference 16. Bond lengths in angstroms, bond angles in degrees.

TABLE 4: Harmonic Frequencies (cm^{-1}) of BrOOBr and ClOOBr[a]

	BrOOBr			ClOOBr		
	MP2 (a)	B3LYP (b)		MP2 (a)	MP2 (c)	B3LYP (b)
OO st A	746	878	OO st	761	764	864
BrO st A	575	504	ClO st	671	652	602
BrOO bnd A	271	230	BrO st	595	574	533
BrOOBr tor A	84	56	ClOO bnd	427	416	412
BrO st B	618	546	BrOO bnd	295	284	280
BrOO bnd B	377	336	ClOOBr tor	101	104	110

[a] Key: (a) AREP/TZ(2df) calculations, this work. (b) 6-311++G(3df,3pd) calculations, ref 9. (c) 6-31G* calculations, ref 8.

Table 3 is, as was the case in the two previous sets of molecules, almost negligible; further, MP2 − B3LYP differences are also very small. In the case of $ClBrO_2$ this agreement between the two different methodologies can be extended to bond angles as well, obtaining discrepancies smaller than 1°, so we can be reasonably confident that we are close to the correct structure for this molecule. Unfortunately, this is not the case with $BrBrO_2$ and $BrClO_2$. In these two species the good agreement found in bond lengths is abruptly spoiled when it comes to comparing angles. Both MP2 and B3LYP calculations carried out in this work seem consistent and provide XYO angles that lie close to 104°. However, surprisingly enough, B3LYP calculations for XYO and OYO in ref 9 (see columns 4 and 10 of Table 3 of the present paper) seem to be somehow switched respect to the values we obtain in this work. This is all the more intriguing if we consider that the two sets of B3LYP results have shown an excellent consistency in the six molecules belonging to the two previous families and also in the case of $ClBrO_2$. On the other hand, atomic charges on the oxygen or halogen atoms at either MP2 or B3LYP levels show no substantial differences that may explain this switching. If we use experimental data for $ClClO_2$, shown in the last column of Table 3, as a test of the reliability of our calculations, it can be seen that our MP2 bond lengths are in excellent agreement with the experimental values and, what is more significant in this case, that MP2 angles agree with the experimental values within an interval smaller than 1°. From the above we can conclude that XYO bond angle must be, in all the three molecules, smaller than OYO angles and that, in light of the concordance of our MP2 data with the experimental values in $ClClO_2$, our geometries are reliable. Finally, we cannot think of any reason $BrBrO_2$ and BrClO2 should be so anomalous in this respect, so we consider the structures summarized in columns 2, 3, 8, and 9 of Table 3 as basically correct for $BrBrO_2$ and $BrClO_2$, respectively.

We summarize in Table 4 our MP2 frequencies for the peroxides along with those in refs 8 and 9 for these molecules. Accurate frequencies are much harder to obtain than geometries; hence they are, in general, somewhat more uncertain unless very high level calculations are carried out. Analyzing data in Table 4 shows that discrepancies between MP2 and B3LYP are always below 15%, except for the OO stretch where B3LYP calculations provide larger values than MP2, which deviate slightly more than the rest of the stretchings, and for the torsional fundamental in BrOOBr where the difference MP2 − B3LYP reaches 33% of the MP2 value. The torsional frequency in this case is very low compared to the other frequencies; besides, torsionals are always difficult to reproduce accurately, so in principle it would be hard to decide whether it should lie closer to 80 cm^{-1} or to 60 cm^{-1}. Fortunately, the torsional fundamental can be calculated[1] in an independent manner from the torsional barrier heights (which we have calculated at a higher level of the theory, CCSD(T), and found to be $V_{cis} = 3596$ cm^{-1} and $V_{trans} = 1916$ cm^{-1}) and from the reduced moment of inertia ($F = 0.6444$ cm^{-1}). The torsional fundamental calculated that way is 89 cm^{-1}, in excellent agreement with our 84 cm^{-1} harmonic value, so we must regard the MP2 torsional as more reliable. In the case of ClOOBr both MP2 results displayed in Table 4 agree quite nicely and differences may well be due to the shorter basis set used in ref 8 compared to the one we use here. Agreement between MP2 and B3LYP is better than it was in the case of BrOOBr, but the same main difference in OO stretches is found.

Frequencies for the XOYO type of molecules are compiled in Table 5. YO stretch frequencies, Y being the internal halogen atom and O the external oxygen, calculated at the MP2/AREP-TZ(2df) level of the theory are systematically larger than the B3LYP values. In the case of BrOClO an experimental result exists[7] that finds the ClO stretch at 991.1 cm^{-1}, closer to the B3LYP result than our MP2 value. An MP2 YO stretch too large might be the case in the other molecules of the family as well. But the most surprising discrepancy in the table is found in the torsional fundamental of BrOClO where, unexpectedly, the B3LYP result is 104 cm^{-1} and MP2 from ref 8 is 169 cm^{-1}. It is not easy to imagine why this torsional that is close to 65 cm^{-1} in BrOBrO and close to 78 cm^{-1} in ClOBrO should be close to 100 cm^{-1} in the case of BrOClO; therefore we look at our 66 cm^{-1} prediction as the closer to the true frequency.

The general agreement between MP2 and B3LYP frequencies in XYO_2 type molecules in Table 6 is reasonably good, the largest differences being in the YO symmetric stretch (Y is the central halogen atom) where they amount to 16% at most. According to the analysis of experimental spectra in ref 7, symmetric and antisymmetric ClO stretches of $BrClO_2$ should appear at 1019.2 and 1193.5 cm^{-1}, respectively, so that both MP2 results in Table 6 seem too large by more than 100 cm^{-1} whereas B3LYP calculations provide more accurate results. Therefore, a similar behavior of MP2 YO stretches in the remaining Y-shaped molecules in the table is not completely unexpected, although we know of no experimental data for them.

TABLE 5: Harmonic Frequencies (cm^{-1}) of XOYO Molecules: BrOBrO, ClOBrO, and BrOClO[a]

	BrOBrO		ClOBrO			BrOClO			
	MP2 (a)	B3LYP (b)	MP2 (a)	MP2 (c)	B3LYP (b)	MP2 (a)	MP2 (c)	B3LYP (b)	exp (d)
YO st	1052	853	1059	1081	859	1206	960	1013	991.1
XO st	608	569	693	683	647	602	742	546	
OY st	420	462	431	406	449	412	598	428	
OYO bnd	261	256	272	262	261	326	367	348	
XOY bnd	163	164	197	187	195	197	232	235	
XOYO tor	63	68	79	77	88	66	169	104	

[a] Key: (a) AREP/TZ(2df) calculations, this work. (b) 6-311++G(3df,3pd) calculations, ref 9. (c) 6-31G* calculations, ref 8. (d) Reference 7.

TABLE 6: Harmonic Frequencies (cm^{-1}) of XYO_2 Molecules: $BrClO_2$, $ClBrO_2$, and $BrBrO_2$[a]

	$BrClO_2$				$ClBrO_2$			$BrBrO_2$	
	MP2 (a)	MP2 (b)	B3LYP (c)	exp (d)	MP2 (a)	MP2 (b)	B3LYP (c)	MP2 (a)	B3LYP (c)
YO st A′	1186	1194	1043	1019.2	1074	1079	900	1066	893
OYO bnd A′	521	485	512		394	382	367	388	364
XYO bnd A′	201	160	201		236	215	238	292	286
XY st A′	398	329	407		327	306	333	177	186
YO st A″	1330	1345	1213	1193.5	1102	1124	955	1092	950
XYO bnd A″	188	138	213		196	185	193	172	174

[a] Key: (a) AREP/TZ(2df) calculations, this work. (b) 6-31G* calculations, ref 8. (c) 6-311++G(3df,3pd) calculations ref 9. (d) Reference 7.

TABLE 7: Heats of Formation ($kcal\ mol^{-1}$) and Absolute Entropies ($kcal\ mol^{-1}\ K^{-1}$)[a]

	$[\Delta H°_f + \Delta E]^b$ (a)		$[\Delta H^0_f + \Delta E]^b$ (b)	isodesmic $\Delta H°_f$ (CCSD(T)) (a)		isodesmic$\Delta H°_f$ (B3LYP) (a)		
	CCSD(T)	B3LYP	B3LYP	0 K	298 K	0 K	298 K	$S°$ (298 K)
$BrBrO_2$	57	53	53	57 (±6)	51(±6)	54	51	0.077
BrOBrO	56	55	55	56(±4)	51(±4)	56	51	0.079
BrOOBr	44	44	46	44(±1)	41(±1)	43	51	0.076
BrOClO	55	54	48	57(±4)	55(±4)	52	50	0.078
$BrClO_2$	56	51	46	58(±6)	52(±6)	51	49	0.074
ClOBrO	50	50	49	52(±6)	49(±6)	51	49	0.076
$ClBrO_2$	45	45	42	46(±6)	42(±6)	42	46	0.074
ClOOBr	38	37	39	39(±2)	38(±2)	39	37	0.075

[a] Key: (a) AREP/TZ(2df) calculations, this work. (b) 6-311++G(3df,3pd) calculations, ref 9. [b] See text for explanation.

Thermochemistry

Isodesmic heats of formation have been obtained for all the species studied in this paper, along with estimates based on the isodesmic heats of the peroxide forms plus the zero-point-energy-corrected (ZPEC) energy differences between isomers. Differences in the results obtained by using these two methods are small in the cases under study here, but the isodesmic approach is in general more trustworthy and allows us to get reasonable estimates of the error ranges in the thermochemical properties obtained. They are summarized in Table 7. The isodesmic reactions used for bromine oxides (Br_2O_2) are

$$\mathrm{BrOOBr + H_2O \rightarrow H_2O_2 + BrOBr} \qquad \text{(I)}$$

$$\mathrm{BrBrO_2 + 2ClBr \rightarrow Br_2 + 2ClBrO} \qquad \text{(II)}$$

$$\mathrm{BrOBrO + ClBr \rightarrow BrOBr + ClBrO} \qquad \text{(III)}$$

In reactions II and III ClBrO is involved, for which no reliable experimental heat of formation is available. We have calculated it at 0 and 298 K from the isodesmic heat of formation for ClOBr (25 kcal mol^{-1} at 0 K and 23 kcal mol^{-1} at 298 K) and our own ZPEC energy difference obtaining 38 ± 3 kcal mol^{-1} at 0 K and 36 ± 3 kcal mol^{-1} at 298 K, which nicely coincides with previous results by Lee[11] (38.0 and 36.1 for 0 and 298 K, respectively). Isodesmic reactions for mixed chlorine−bromine dioxides (XYO_2) are

$$\mathrm{2ClOOBr + 2H_2O \rightarrow 2H_2O_2 + ClOCl + BrOBr} \qquad \text{(IV)}$$

$$\mathrm{ClBrO_2 + Br_2 \rightarrow ClBr + BrBrO_2} \qquad \text{(V)}$$

$$\mathrm{BrClO_2 + Br_2 \rightarrow ClBr + BrBrO_2} \qquad \text{(VI)}$$

$$\mathrm{ClOBrO + ClBr \rightarrow ClOBr + ClBrO} \qquad \text{(VII)}$$

$$\mathrm{BrOClO + Cl_2 \rightarrow ClBrO + ClOCl} \qquad \text{(VIII)}$$

where all the necessary species involved in reactions IV through VIII have well-determined heats of formation,[12,13] except ClBrO, as was the case above. A number of other possible isodesmic schemes have been considered but not used because the larger errors in the needed experimental enthalpies lead to larger uncertainties in the calculated values for the XYO_2 species. Other heats of formation used for the discussions in this paper are 31.8 and 30.0 kcal mol^{-1} at 0 and 298 K, respectively, for BrO, and 22.08 kcal mol^{-1} at 0 K and 24.19 kcal mol^{-1} at 298 K for ClO taken from ref 12. Absolute entropies for these two species at 298 K used are 55.6 cal K^{-1} mol^{-1} for BrO and 54.2 cal K^{-1} mol^{-1} from the same reference.

Calculations of the heat of formation have been carried out at CCSD(T)/AREP-TZ(2df) and B3LYP/AREP-TZ(2df) levels using always MP2 optimized geometries and frequencies, and the results at 0 and 298 K are contained in Table 7. According to CCSD(T) results, the most stable species, with respect to its elements in their standard states, in the family of Br_2O_2 is the peroxide form: 44 ± 1 kcal mol^{-1} at 0 K, BrOBrO and $BrBrO_2$ showing essentially the same enthalpy of formation. In the mixed bromine−chlorine oxides family the peroxide form is again the most stable 39 ± 2 kcal mol^{-1} at 0 K, followed by $ClBrO_2$, ClOBrO, and $BrClO_2$, which have approximately the same value of the heat of formation as BrOClO. This ordering is basically maintained when B3LYP calculations are considered and even if CCSD(T) plus ZPEC energy differences are used to make the comparison; however, it disagrees with previous B3LYP ZPEC calculations[9] that propose $BrClO_2$ as lower in energy than ClOBrO and BrOClO. Even though we have adopted very conservative error estimates, it seems rather clear from our calculation of the relative energies and heats of formation that species containing internal bromine atoms (OBrO) tend to be favored with respect to those containing chlorine internal atoms, as was to be expected from chemical intuition and as is concluded from the discussion in the previous section. That is also the case in triatomics when comparing ClBrO and BrClO where we find, at the CCSD(T) level, the former to be around 8 kcal mol^{-1} more stable than BrClO, which agrees again with previous calculations by Lee.[11]

As is well-known, it has been hypothesized that transient species of the type XOOY and XOYO may be formed in the reaction of halogen oxides such as ClO and BrO, producing Br + ClOO that further decomposes into Cl + O_2 (following schemes in ref 14), so it is not only the relative stabilities that are important here but also the Gibbs free energy of formation of these species that provides an indication of which processes may be expected to occur. Absolute entropies at room temperature (included in Table 7) and at stratospheric temperature (200 K) for mixed bromine−chlorine dioxides have been calculated and the Gibbs free energies for the reactions of formations from ClO + BrO determined. We have found that reaction leading to ClOOBr is obviously spontaneous at 298 K ($\Delta G_f = -6$ kcal mol^{-1}) and, in sight of the values of the heats of formation in Table 7, also at 200 K. This is more unclear in the cases of $ClBrO_2$ ($\Delta G_f = -2$ kcal mol^{-1}) and ClOBrO ($\Delta G_f = 5$ kcal mol^{-1}), where the estimated uncertainties in heats of formation may change the actual sign of ΔG. However, the formation of $BrClO_2$ ($\Delta G = 8$ kcal mol^{-1}) and BrOClO ($\Delta G = 10$ kcal mol^{-1}) does not occur either at 298 K or at 200 K, since in these cases $\Delta G > 0$, even allowing for our conservative estimate of errors. We conclude that intermediate BrOClO proposed[14] as responsible for the occurrence of OClO is not to be expected from reaction of the halogen monoxides. Also $BrClO_2$, for which no direct evidence of existence was found,[14] cannot be formed, whereas ClOO and ClBr are in fact compatible with ClOOBr and $ClBrO_2$. Johnsson et al.[7] have suggested that BrOClO can be formed by adding bromine to OClO.

As for the BrO self-reaction, the value of ΔG_f for BrOOBr is clearly negative at all temperatures (-9 kcal mol^{-1} at 298 K) and values for BrOBrO and $BrBrO_2$ are very close to 1 kcal mol^{-1}. Considering again the error estimates for the heats of formation, BrO + BrO might produce these species, although it is thought[15] that BrOBrO does not form whereas the observed BrOO may come from the corresponding peroxide.

Conclusions

As a summary of the discussion above, we can conclude that bond lengths are reasonably well determined by either B3LYP or MP2 methods, though comparisons with experimental data in ClOOCl display some superiority of MP2. However, there are clear differences in the bond angles, especially in dihedral angles that are more difficult to determine accurately. Comparisons with experimental angles in the case of ClOOCl clearly favor MP2 dihedrals, but the most notorious differences are found in the case of hypervalent molecules XOYO, where B3LYP bond angles are difficult to conciliate with any qualitative or semiquantitative analysis based on atomic charges, whereas MP2 results seem consistent with them all. Finally, our B3LYP and MP2 bond angles in the case of XYO_2 are in good agreement, displaying a sharp difference with the values in ref 9 for $BrBrO_2$ and $BrClO_2$. We feel inclined to trust better the MP2 optimized geometries, especially when dealing with such difficult cases as XOYO or XYO_2.

As for frequencies, we conclude that some deficiencies seem to appear in the MP2 prediction of YO stretches that are not present in the B3LYP calculations analyzed here, but on the other hand MP2 torsionals seem more reliable.

Relative energies and heats of formation at 0 and 298 K have been calculated for the mixed chlorine−bromine containing species and for the members of the Br_2O_2 family. The B3LYP method tends to provide slightly smaller values for these properties than CCSD(T), but in essence the same results are obtained. From the heats of formation and absolute entropies it is found that only ClOOBr, and perhaps $ClBrO_2$, are likely to be formed from ClO + BrO, especially at stratospheric temperatures, whereas in the dibromine dioxides family the only clear candidate is the peroxide form, in agreement with experimental evidence.

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